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**2007 CBIS**

# **Atmospheric Chemistry of Toxic Industrial Chemicals**

**11 Jan 2007**

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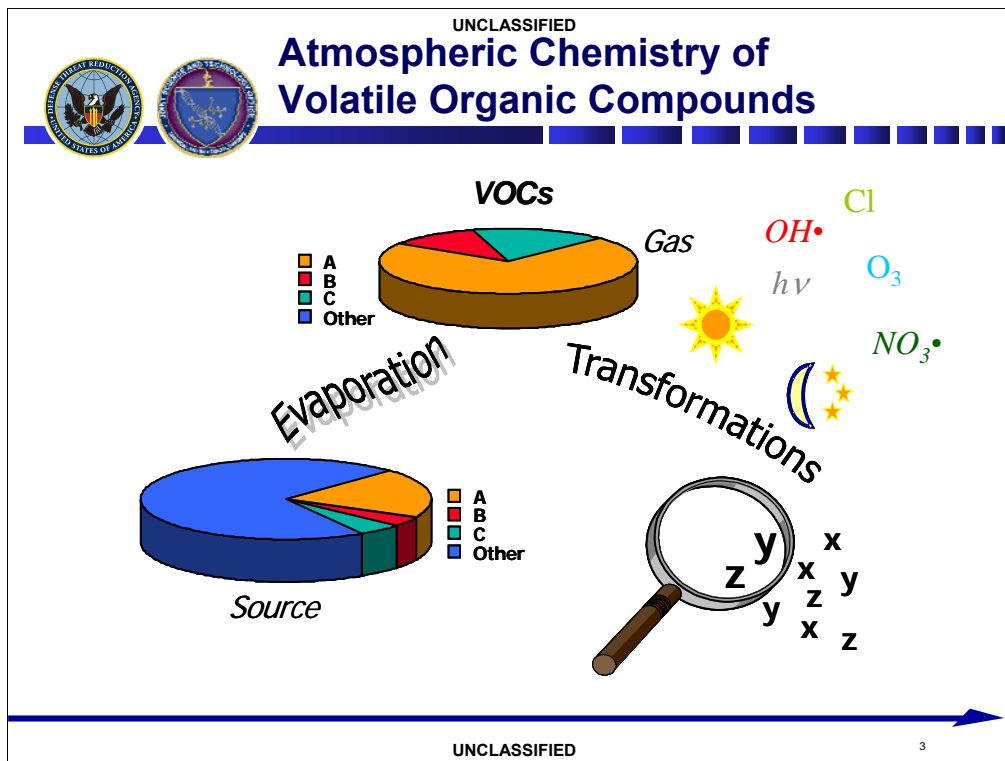
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## Overview

- **Introduction to Atmospheric Chemistry**
- **Importance to Dispersion Modeling**
- **TIC Kinetics**
- **Past, Present, Future**

In this presentation I'll introduce you to atmospheric chemistry, show an example of how our results are used, and the impact that atmospheric chemistry has on the outcome. Then I'll discuss the kinetic data for atmospheric TIC reactions that we've been collecting and conclude with a discussion of where we've been and where we're headed in the future.

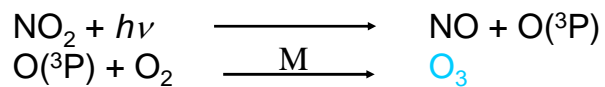


This cartoon depicts the dynamic nature of the atmosphere. While volatile chemicals released from a source are transported and dispersed through the troposphere they are subjected to chemical reactions along the way. In the case of volatile organic compounds, reaction with the hydroxyl ( $OH^\bullet$ ) radical during the day is the primary loss mechanism for removal of the VOC from the atmosphere. At night, when  $OH$  concentrations decrease, the nitrate ( $NO_3$ ) radical can play an important role in transformation of the VOC. The reaction with ozone ( $O_3$ ) is typically slower but can be important for unsaturated molecules (e.g. the alkenes that will be discussed later). Reactions with chlorine atoms ( $Cl$ ) can occur in early morning hours, shortly after dawn, when a burst of  $Cl$  is released near coastal areas. Other reactions can also occur such as direct photolysis of the molecule. All of these reactions transform the parent compound into daughter products whose identity is important to understand. This dynamic process leads to two important questions: (1) How fast do these reactions occur? (what are the kinetics of the reaction?); and (2) What is the reaction mechanism? (what are the products and their yield?)

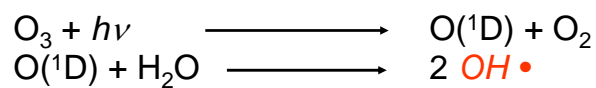


## Tropospheric Oxidant Formation

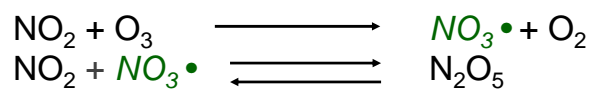
### Ozone



### OH Radical



### NO<sub>3</sub> Radical

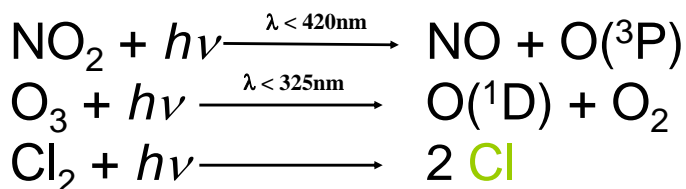


This chart shows the reactions involved in generation of the typical oxidants in the troposphere.

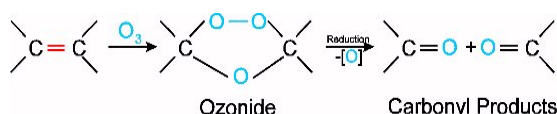


## Tropospheric Transformations

### Photolysis



### Ozonolysis

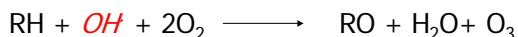
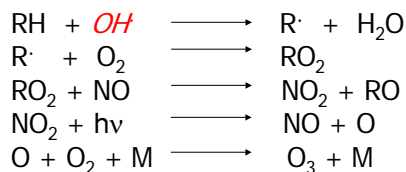


Typical  $[\text{O}_3] =$   
 $2.5 \times 10^{12}$   
 molecules/cm<sup>3</sup>  
 100 ppb @STP

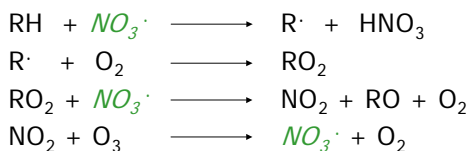
On the top are some examples of chemicals that can be photolyzed directly in the troposphere by sunlight, including chlorine which generates the very reactive chlorine atom. On the bottom is an example of ozone reacting with ethene to form carbonyl compounds. While reaction with ozone is typically slower than with the radical species (OH, NO<sub>3</sub>), its concentration is several orders of magnitude higher (as you can compare on the next chart) so the effective rate of reaction observed can be significant with these types of molecules.



## Important Radical Reactions

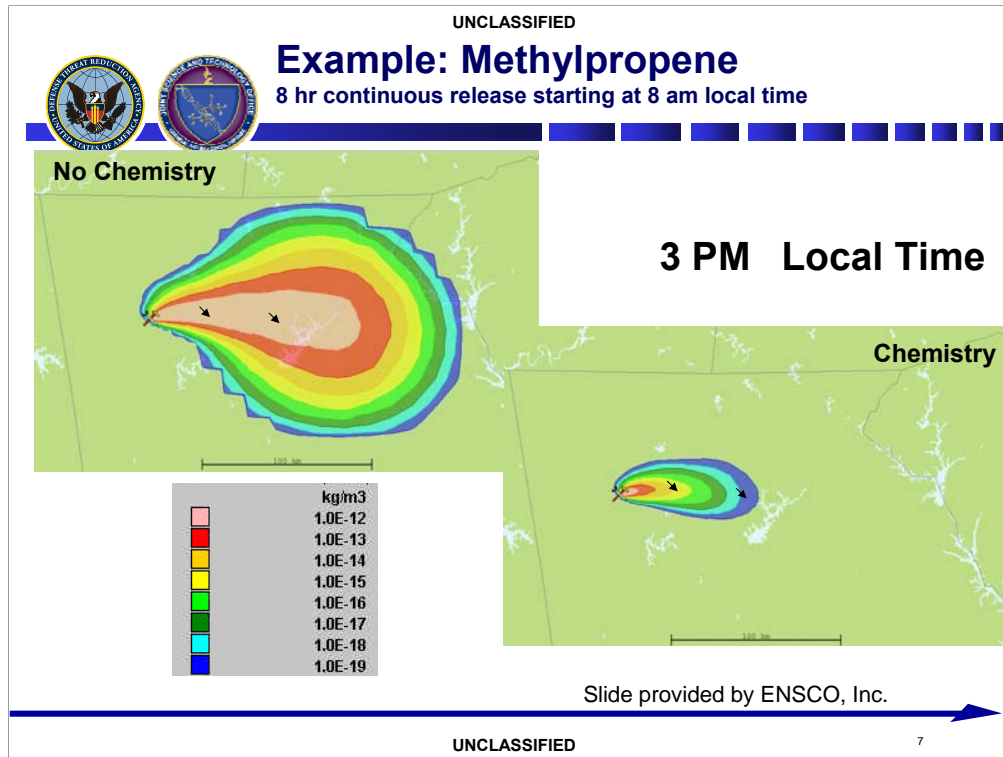


Typical  $[\text{OH}] =$   
 $1 \times 10^6$  molecules/cm<sup>3</sup>  
 $3.72 \times 10^{-2}$  ppt @STP



Typical  $[\text{NO}_3] =$   
 $2.5 \times 10^8$   
 molecules/cm<sup>3</sup>  
 9.3 ppt @STP

Reactions of OH with organic molecules typically proceed through a hydrogen abstraction process from the VOC to form water and an organic radical. The organic radical goes through a series of subsequent reactions before forming a stable (not a radical) product. OH reaction with the double bond in unsaturated compounds proceeds through an addition mechanism. VOC reaction with NO<sub>3</sub> are similar to reaction with OH where NO<sub>3</sub> abstracts a hydrogen to form nitric acid and an organic radical followed by subsequent reactions. You can see that the concentrations of these radical species are 4 – 6 orders of magnitude lower than ozone yet these are the dominant day and night reactions due to very rapid reaction kinetics.



kg/m<sup>3</sup>

1.0E-12

1.0E-13

1.0E-14

1.0E-15

1.0E-16

1.0E-17

1.0E-18

1.0E-19

7

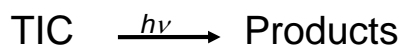
This is an example of the atmospheric chemistry model that we have incorporated into the Second-Order Closure Integrated Puff (SCIPUFF) model. The two SCIPUFF plume outputs depicted on this slide are identical except that the lower right is accounting for the reactivity of 2-methyl propene in the atmosphere. I've placed two arrows on the map to help you get a reference point. You can clearly see the importance of including the chemistry by looking at the arrow on the right. The absolute numbers indicated by the contours are not important. What is important is the seven orders of magnitude difference in the predicted concentrations.





## Reaction Kinetics

- Photolysis:



$$-d[\text{TIC}]/dt = k_p[\text{TIC}], k_p \text{ in sec}^{-1}$$

- Bimolecular reaction:



$$-d[\text{TIC}]/dt = k_{\text{OH}} [\text{TIC}][\text{OH}],$$

$$k_{\text{OH}} \text{ in cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$$

We need to know the reactivity of a TIC with the various oxidants, sunlight, etc. to be able to model its degradation in SCIPUFF. You can write the rate equations for photoysis or for a bimolecular reaction as shown. Since the concentration of the oxidant in bimolecular reactions is constant (and presumably known) in the atmosphere, you only need to know the concentration of your TIC and the rate constant to be able to calculate the decay rate of the TIC. We want to model the TIC concentration so we need to know the rate constants. We can obtain them via the literature if they exist or we have to determine them experimentally.



## Example of TIC Kinetic Data

Name	CAS #	Reaction with OH Radicals	Reaction with Ozone	Reaction with NO3 Radicals
		Reaction Rate, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Reaction Rate, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Reaction Rate, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$
1,1-dichloroethylene	75-35-4	$8.1 \times 10^{-12}$	$3.7 \times 10^{-21}$	$1.23 \times 10^{-15}$
1,1-difluoroethylene	75-38-7	$4.0 \times 10^{-12}$	$1.4 \times 10^{-19}$	
2-methylpropene	115-11-7	$5.14 \times 10^{-11}$	$1.13 \times 10^{-17}$	$3.32 \times 10^{-13}$
acetaldehyde	75-07-0	$1.5 \times 10^{-11}$	$<6 \times 10^{-21}$	$2.7 \times 10^{-15}$
acetylene	74-86-2	$7.80 \times 10^{-13}$	$1 \times 10^{-20}$	$<1 \times 10^{-16}$
carbon monoxide	630-08-0	$2.08 \times 10^{-13}$		$<4 \times 10^{-19}$
chloroethylene	75-01-4	$2.36 \times 10^{-12}$		$2.93 \times 10^{-16}$
chloromethane	74-87-3	$4.2 \times 10^{-14}$		
diethyl ether	60-29-7	$1.3 \times 10^{-11}$		
dimethyl ether	115-10-6	$2.8 \times 10^{-12}$		$<3 \times 10^{-15}$
dimethyl sulphide	75-18-3	$4.80 \times 10^{-12}$	$<1.0 \times 10^{-18}$	$1.1 \times 10^{-12}$
dimethylamine	124-40-3	$6.54 \times 10^{-11}$	$2.61 \times 10^{-18}$	
ethanethiol	75-08-1	$4.64 \times 10^{-11}$		$9.87 \times 10^{-13}$
ethyl vinyl ether	109-92-2	$4.04 \times 10^{-11}$	$1.54 \times 10^{-16}$	
ethylamine	75-04-7	$2.77 \times 10^{-11}$	$2.76 \times 10^{-20}$	
ethylene oxide	75-21-8	$8 \times 10^{-14}$		
hydrogen cyanide	74-90-8	$3.0 \times 10^{-14}$		
hydrogen sulfide	7783-06-4	$4.7 \times 10^{-12}$		$<1 \times 10^{-15}$
isoprene	78-79-5	$1.0 \times 10^{-10}$	$1.27 \times 10^{-17}$	$7.0 \times 10^{-13}$

This chart is just a sampling of the data we have been collecting for volatile TICs. Of importance here is the relative order of magnitude difference for the type of oxidant and type of chemical. For example, OH rate constants range from  $10^{-10}$  to  $10^{-14}$ , O3 from  $10^{-16}$  to  $10^{-21}$ , and NO3 from  $10^{-13}$  to  $10^{-19}$ . You can see that OH rate constants are typically much faster than ozone or NO3 but keep in mind that the atmospheric concentrations of NO3 and ozone are about 2 and 6 orders of magnitude higher in concentration than OH, respectively. You will also note that the unsaturated and organosulfur compound NO3 rate constants are considerably faster than the other NO3 rate constants. This means that these compounds undergo significant degradation even during the night.



## Atmospheric Lifetime

- Bimolecular reaction:



$$-d[\text{TIC}]/dt = k_{\text{OH}} [\text{TIC}][\text{OH}],$$

$k_{\text{OH}}$  in  $\text{cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$

- Lifetime ( $\tau$ ) Calculation

- Time for the TIC to decrease to 1/e of its initial value
- Oxidant [OH] assumed to be constant  
@  $1 \times 10^6 \text{ molecules cm}^{-3}$
- $\tau = 1/(k_{\text{OH}} * [\text{OH}])$
- Example where  $k_{\text{OH}} = 10 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$   
 $\tau = 1/(10 \times 10^{-12} * [1 \times 10^6])$   
 $\tau = 1 \times 10^5 \text{ sec} \div 86,400 \text{ sec/day} \sim 1.2 \text{ days}$

Atmospheric lifetime expressed as 1/e is analogous to half life and may be a little easier to grasp the reactivity of some of these molecules. Here we go through the calculation of the lifetime for a compound having an OH rate constant of  $10 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$  arriving at an atmospheric lifetime of about 1.2 days. I go through this exercise to show you where the numbers on the next chart come from.



## Estimated Atmospheric Lifetimes

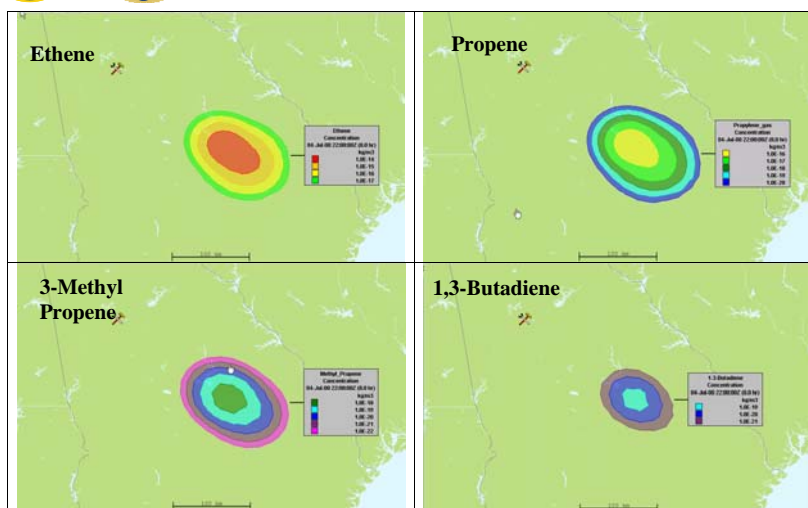
Organic	OH [ $1 \times 10^6 \text{ cm}^{-3}$ ], 0.038ppt	O <sub>3</sub> [ $2.5 \times 10^{12} \text{ cm}^{-3}$ ], 100ppb	NO <sub>3</sub> [ $1.3 \times 10^9 \text{ cm}^{-3}$ ], 50ppt	Cl [ $1 \times 10^4 \text{ cm}^{-3}$ ], 0.00038ppt
<i>n</i> -Butane	5 days	≥ 1300 yr	205 days	5 days
<i>trans</i> -2-Butene	4.3 hours	36 min	35 min	~4 days
Acetylene	14 days	≥ 400 days	≥ 188 days	~22 days
Toluene	2 days	≥ 400 days	138 days	20 days
Formaldehyde	1.2 days	≥ 463 days	16 days	16 days
Hydrogen sulfide	2.5 days	-	≥ 213 days	-

Table derived from Finlayson-Pitts & Pitts, 2000

Estimated lifetimes of TICs derived from Finlayson-Pitts and Pitts are shown in the chart. The oxidant concentration used to perform the calculation is given at the top of each column. You can see the wide variability in lifetimes and; therefore, the relative reactivity of the chemicals. Of particular interest is *trans*-2-butene which has lifetimes with ozone and NO<sub>3</sub> under forty minutes while its lifetime with OH is 4.3 hours. This is one of the rare cases where ozone or NO<sub>3</sub> reactions with an organic molecule are more important than reaction with OH. The take home message here is that knowing the reactivity of the TIC is critical to being able to accurately predict its degradation within a transport and dispersion plume.



## Calculated Plume is TIC Dependent



Slide provided by ENSCO, Inc.

The four SCIPUFF outputs shown on this slide are all modeling the exact same release. The only difference is the chemical that is being released. Again you can clearly see that the reactivity of the chemical leads to very different predictions.



## Past, Present & Future

- Atmospheric chemistry plays significant role in dispersion of many TICs
- Kinetic data necessary to model reactivity
- Degrade algorithm developed for SCIPUFF
- Model optimization and sensitivity studies underway
- Chamber experiments for degrade algorithm validation being designed
- Heterogeneous aerosol interactions need addressing

I've shown you the importance of accounting for atmospheric reactions within transport and dispersion models and how we use kinetic data to model the reactivity within the degrade algorithm we've developed for SCIPUFF. We are currently optimizing the performance of "degrade" and performing sensitivity analyses to assess which input parameters require the most accurate data. We are designing chamber experiments to validate the model's accuracy in terms of predicting chemical reactivity within the plume. Finally, what we have discussed thus far only considers gas-phase reactions that occur in the troposphere. We have sufficient data to suggest that heterogeneous interaction with atmospheric aerosols is equally important in savaging chemicals from the atmosphere and should be addressed in the future.



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